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(11) **EP 1 260 608 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
27.11.2002 Bulletin 2002/48

(51) Int Cl.7: **C23C 28/00**

(21) Application number: **01112646.3**

(22) Date of filing: **25.05.2001**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**  
Designated Extension States:  
**AL LT LV MK RO SI**

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(54) **Method of depositing a MCrAlY bond coating**

(57) It is disclosed a method of depositing a bond MCrAlY-coating to a surface of an article for increasing the roughness for enhanced TBC adhesion. First, an inner layer on top of the surface of the article consisting of  $\gamma\gamma$ -MCrAlY is deposited using powder in the size

range from 5 to 65  $\mu\text{m}$ . Second, an outer bond coating layer on top of the inner layer consisting of  $\beta$ -NiAl or  $\gamma$ / $\beta$ -MCrAlY or  $\gamma\gamma$ -MCrAlY is deposited using powder in the size range from 30 to 125  $\mu\text{m}$ .

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## Description

### FIELD OF INVENTION

[0001] The invention relates to a method of depositing the bond coating according to the preamble of claim 1.

### STATE OF THE ART

[0002] Components designed for the use in the area of high temperature, e.g. blades or vanes of a gas turbine, are usually coated with resistant coatings. The coating protects the base material against corrosion and oxidation due to the thermal effect of the hot environment and consists of an alloy mostly using the elements Al and Cr. Most turbine components are coated for the protection from oxidation and/or corrosion with, for example, a MCrAlY coating (base coat) and some are also coated with a thermal barrier coating (TBC) for thermal insulation. MCrAlY protective overlay coatings are widely known in the prior art. They are a family of high temperature coatings, wherein M is selected from one or a combination of iron, nickel and cobalt. As an example US-A-3,528,861 or US-A-4,585,481 are disclosing such kind of oxidation resistant coatings. US-A-4,152,223 as well discloses such method of coating and the coating itself. Besides the  $\gamma\beta$ -MCrAlY-coating, there is another class of overlay MCrAlY coatings which are based on a  $\gamma\gamma'$ -gamma/gamma prime-structure. The advantages of  $\gamma\gamma'$ -coatings is that they have a negligible thermal expansion mismatch with alloy of the underlying turbine article. For higher thermal fatigue resistance the  $\gamma\gamma'$ -coating are more convenient compared to the  $\gamma\beta$ -type of MCrAlY-coatings. A higher thermal fatigue resistance in coatings is most desirable since failure of the most turbine blades and vanes at elevated temperature is typically thermal fatigue driven.

[0003] Among  $\gamma\gamma'$ -coatings and  $\gamma\beta$ -coatings, the field of  $\gamma\beta$ -coatings have been an active area of research and a series of patents has been issued. E.g. a Ni-CrAlY coating is described in US-A-3,754,903 and a CoCrAlY coating in US-A-3,676,058. US-A-4,346,137 discloses an improved high temperature fatigue resistance NiCoCrAlY coating. US-A-4,419,416, US-A-4,585,481, RE-32,121 and US-A-4,743,514 describe MCrAlY coatings containing Si and Hf. US-A-4,313,760 discloses a superalloy coating composition with good oxidation, corrosion and fatigue resistance.

[0004] In contrast to the  $\gamma\beta$ -coatings, the  $\gamma\gamma'$ -type of MCrAlY coatings, known e.g. from US-A-4,973,445, are relatively new. The unique feature of this type of  $\gamma\gamma'$ -coatings is that their thermal expansion mismatch is close to zero in combination with a high ductility, what make these coatings more resistant to thermal fatigue. However the limitations are the low aluminum content and hence their low reservoir of aluminum.

[0005] Furthermore, in the state of the art Thermal Barrier-Coatings (TBC) are known from different pat-

ents. US-A-4,055,705, US-A-4,248,940, US-A-4,321,311 or US-A-4,676,994 disclose a TBC-coating for the use in the turbine blades and vanes. The ceramics used are yttria stabilized zirconia and applied by plasma spray (US-A-4,055,705, US-A-4,248,940) or by electron beam process (US-A-4,321,311, US-A-4,676,994) on top of the MCrAlY bond coat.

[0006] One major disadvantage of  $\gamma\gamma'$ -type of MCrAlY coatings is that due to the low aluminum content they do not form a continuous alumina film at temperatures below 1000°C what leads to a problem with the bonding adherence with the TBC. Therefore US-A-5,894,053 developed a process for applying a particulate metallic adhesion layer for ceramic thermal barrier coatings to metallic components. The essential content of the patent is a process of forming a roughened surface by applying particulate materials on the surface using binder, principally soldering power. The disadvantages of the process are the depression of the melting point of coating by soldering, a potential fatigue debits of the bond coating and the fluxing of the Thermally Grown Oxide (TGO) by the soldering material. In addition, there is no hint within US-A-5,894,053 of how to enhance the alumina forming capacity of a  $\gamma\gamma'$ -type of MCrAlY coating.

### SUMMARY OF THE INVENTION

[0007] It is object of the present invention to find a method of depositing a  $\gamma\gamma'$ - bond coating resisting to crack during thermal cycling prevalent in the engine. Another object of the present invention is to provide a bond coating with an enhanced surface roughness for an increased TBC adhesion. Yet another object of the present invention is to provide a layer on top of the coating which forms an alumina TGO readily in the engine or by prior heat treatment.

[0008] According to the invention a method of depositing a bond MCrAlY-coating according to the preamble of claim 1 was found, wherein before the TBC is applied, an inner layer on top of the surface of the article consisting of  $\gamma\gamma'$ -MCrAlY is deposited using powder in the size range from 5 to 65  $\mu\text{m}$  and an outer bond coating layer on top of the inner layer, which outer layer is more coarse than the inner layer and consisting of  $\beta$ -NiAl or  $\gamma\beta$ -MCrAlY or  $\gamma\gamma'$ -MCrAlY, is deposited using powder in the size range from 30 to 125  $\mu\text{m}$ . Preferably the inner layer on top of the surface of the article is deposited using powder in the size range from 15 to 50  $\mu\text{m}$ , most preferable below 30  $\mu\text{m}$ , and the outer layer on top of the inner layer is deposited using powder with a particle size from 35 to 90  $\mu\text{m}$ .

[0009] Due to the fact that the outer bond coating layer is deposited using a powder which is more coarse than the underlying inner layer, the surface roughness and the TBC adherence is significantly increased.

[0010] For the formation of  $\text{Al}_2\text{O}_3$  prior to TBC-deposition the deposited bond coating can be heat-treated at temperatures up to 1140°C, which is possible in air, ar-

gon, vacuum or an environment conductive to form the alumina scale, which further increases the TBC adherence. Beside that the heat-treatment stabilizes the coating. To form the alumina scale the outer layer can as well be aluminized using a pack or an out of pack gas phase diffusion process.

[0011] The coating can be applied by a galvanic or plasma spray or any other conventional Plasma Vapor Deposition (PVD) method used for deposition of overlay and bond coatings.

#### DETAILED DESCRIPTION OF INVENTION

[0012] It is disclosed a bond MCrAlY-coating of an article for the use within a high temperature environment for the protection of the base alloy of turbine blades and vanes.

[0013] According to the invention the bond MCrAlY-coating consists of two different layers. An inner layer on top of the surface of the article consisting of MCrAlY with a structure of  $\gamma\gamma$ . The inner layer is deposited with a powder in the size range from 5 to 65  $\mu\text{m}$ . An outer layer on top of the inner layer consists of  $\beta$ -NiAl,  $\gamma$ / $\beta$ -MCrAlY or even of  $\gamma\gamma$ -MCrAlY. But, in contradiction to the inner layer, the outer layer is deposited with a coarse powder in the size range from 30 to 125  $\mu\text{m}$ . A ceramic coating such as TBC is deposited on top of the outer bond coating layer. Due to the fact that the outer bond coating layer is deposited using a powder which is more coarse than the underlying inner layer, the surface roughness and the TBC adherence is significantly increased.

[0014] Preferably the inner layer on top of the surface of the article is deposited using powder in the size range from 15 to 50  $\mu\text{m}$ , most preferable below 30  $\mu\text{m}$ , and the outer layer on top of the inner layer is deposited using powder with a particle size from 35 to 90  $\mu\text{m}$ .

[0015] The technology disclosed in this invention directly translates lifetime improvement by increasing TBC adherence due to enhanced surface roughness of the external layer. The composition microstructure of the outer layer can also be independently adjusted to allow formation of an alumina scale beneath the TBC. An example is the use of  $\beta$ -NiAl or  $\gamma\beta$ -MCrAlY or even  $\gamma\gamma$ -MCrAlY as the outer layer. In addition the inner layer of  $\gamma\gamma$ -MCrAlY comprises one or a combination of Y, Hf, Zr and Si with (wt-%) 0.01 - 5% Y+Hf+Zr+Si and one or a combination of Ta, Fe, Ga, Mg and Ca.

[0016] The outer layer may consist of a  $\beta$ -NiAl outer layer and the  $\beta$ -NiAl may contain aluminum from about 20 to 33 wt.-%, which falls in the single phase range of NiAl phase diagram. The  $\beta$ -NiAl has a high oxidation resistance which can be further enhanced by a minor elemental addition. This is known e.g. from the patents US-A-4,610,736, US-A-5,116,438, US-A-5,516,380, US-A-5,116,691, US-A-4,961,905, US-A-4,478,791 or US-A-5,215,831. A possible content of the inner layer of  $\beta$ -NiAl is (wt-%) 0.001 - 0.5% Y, 0.001 - 0.5% Hf, 0.001

- 0.5% Zr, 0.1 - 1.5% Si, 0 - 1.0% Ca, 0 - 1.0% Mg, 0 - 4% Ga, 0 - 4% Fe, 0.1 - 4.0% Ta.

[0017] Optionally, for the formation of  $\text{Al}_2\text{O}_3$  prior to TBC-deposition, the deposited bond coating may be heat-treated at temperatures of up to 1140°C, which can be done in air, argon, vacuum or an environment conductive to form the alumina scale, which further increases the TBC adherence. Beside that the heat-treatment stabilizes the microstructure of the coating. Thereby, the 1140°C heat-treatment has been found to be most advantageous to fully stabilize the microstructure. The 1140°C heat-treatment can also be used to pre-form alumina prior to TBC deposition. For the formation of the aluminum scale the outer layer can be aluminized using a pack or an out of pack gas phase diffusion process.

[0018] The coating can be applied by a galvanic or plasma spray or any other conventional PVD method used for deposition of overlay and bond coatings.

#### Claims

1. A method of depositing a bond MCrAlY-coating to a surface of an article for increasing the roughness for enhanced adhesion of a Thermal-Barrier-Coating (TBC), wherein before the TBC is applied,
  - an inner layer on top of the surface of the article consisting of  $\gamma\gamma$ -MCrAlY is deposited using powder in the size range from 5 to 65  $\mu\text{m}$  and
  - an outer bond coating layer on top of the inner layer, which outer layer is more coarse than the inner layer and consisting of  $\beta$ -NiAl or  $\gamma\beta$ -MCrAlY or  $\gamma\gamma$ -MCrAlY, is deposited using powder in the size range from 30 to 125  $\mu\text{m}$ .
2. The method of depositing a bond MCrAlY-coating according to claim 1, wherein the inner layer on top of the surface of the article is deposited using powder in the size range from 15 to 50  $\mu\text{m}$  and the outer layer on top of the inner layer is deposited using powder in the size range from 35 to 90  $\mu\text{m}$ .
3. The method of depositing a bond MCrAlY-coating according to claim 1, wherein the inner layer on top of the surface of the article is deposited using powder in the size range below 30  $\mu\text{m}$ .
4. The method of depositing a bond MCrAlY-coating according to any of the claims 1 to 3, wherein the deposited bond coating is heat-treated at a temperature up to 1140 °C prior to the TBC deposition.
5. The method of depositing a bond MCrAlY-coating according to claim 4, wherein the deposited bond coating is heat-treated in air, argon, vacuum or an environment conductive to form an alumina scale prior to the TBC deposition.

6. The method of depositing a bond MCrAlY-coating according to claim 1, wherein the outer layer is aluminized using a pack or an out of pack gas phase diffusion process.

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7. The method of depositing a bond MCrAlY-coating according to claim 1, wherein the different layers are deposited by using a galvanic or a plasma spray or any PVD method used for deposition of bond coatings.

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## EUROPEAN SEARCH REPORT

Application Number

EP 01 11 2646

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	WO 99 43861 A (GEN ELECTRIC) 2 September 1999 (1999-09-02) * the whole document *	1-7	C23C28/00
A	US 5 579 534 A (ITOH MASAYUKI ET AL) 26 November 1996 (1996-11-26) * claims 1,6-8 *	1	
A	DATABASE INSPEC 'Online! INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB; GUDMUNDSSON B ET AL: "Structure formation and interdiffusion in vacuum plasma sprayed CoNiCrAlY coatings on IN738LC" Database accession no. 3204625 XP002181289 * abstract * & MATERIAL SCIENCE AND ENGINEERING, APRIL 1988, SWITZERLAND, vol. 100, pages 207-217, ISSN: 0025-5416	1	
D,A	US 4 973 445 A (SINGHEISER LORENZ) 27 November 1990 (1990-11-27) * the whole document *	1	C23C
A,D	US 4 313 760 A (DARDI LOUIS E ET AL) 2 February 1982 (1982-02-02) * the whole document *	1	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>26 October 2001</b>	Examiner <b>Ceulemans, J</b>
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 1503 03/82 (PatCat)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 11 2646

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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26-10-2001

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 9943861	A	02-09-1999	EP	1076727 A1	21-02-2001
			WO	9943861 A1	02-09-1999
US 5579534	A	26-11-1996	JP	8041619 A	13-02-1996
US 4973445	A	27-11-1990	DE	3740478 C1	19-01-1989
			DE	3882024 D1	29-07-1993
			EP	0318803 A1	07-06-1989
US 4313760	A	02-02-1982	CA	1153584 A1	13-09-1983
			CA	1170862 A1	17-07-1984
			CA	1169267 A1	19-06-1984
			DE	3010608 A1	11-12-1980
			DE	3030961 A1	12-03-1981
			DE	3030962 A1	12-03-1981
			FR	2457907 A1	26-12-1980
			FR	2463191 A1	20-02-1981
			FR	2463192 A1	20-02-1981
			GB	2056491 A ,B	18-03-1981
			GB	2058835 A ,B	15-04-1981
			JP	1370702 C	25-03-1987
			JP	56108850 A	28-08-1981
			JP	61036061 B	16-08-1986
			JP	1403223 C	28-09-1987
			JP	56108851 A	28-08-1981
			JP	62003221 B	23-01-1987
			US	4339509 A	13-07-1982
			US	4764225 A	16-08-1988
			GB	2056487 A ,B	18-03-1981
			JP	55161041 A	15-12-1980

EPO FORM P459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82